

Photolytic and Photocatalytic Recreational Water Treatment

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Abstract. Disinfection is one of the most important steps during recreational water treatment. Nevertheless, disinfection by-products are formed by conventional disinfectants, which pose several health threats. The concentration of disinfection by-products can be decreased by photolytic and photocatalytic treatment. Medium-pressure mercury lamp, UV-LEDs and solar irradiation were investigated and evaluated considering emitted wavelength, light intensity and operational costs. It was found that medium-pressure mercury lamps are superior for photolytic and photocatalytic recreational water treatment.

Keywords: Photocatalysis, water purification, DBP.

1. Introduction

Usage of swimming pools shall promote recreation and healthiness to swimmers. Preventing microorganism related diseases, disinfection with chlorine is an indispensable treatment step. Besides killing or rendering microorganisms inert, the disinfectant also reacts with organic and inorganic compounds in the water forming disinfection by-products (DBPs). The precursors of these DBPs include natural organic matter and all other substances introduced by bathers like, sweat, urine or ointments and creams. Today, over 600 DBPs have been identified, of which the most are summarized in the review of Hrudey [1]. Proceeding research has shown that DBPs act adversely on human health. They can cause tissue irritation, they can act as sensitizer or they were found to be mutagenic or carcinogenic [2]. Trihalomethanes (THMs) were the first reported DBPs and are nowadays commonly regulated DBPs for water treatment [1]. Approximately 25% of the halogenated DBPs are THMs and haloacetic acids [2]. Another well known DBP is trichloramine, which is the source of "chlorine" smell and tissue irritation [3]. Richardson et al. [2] provide an extensive overview of mutagenic and carcinogenic DBPs, like oxyhalides, halonitromethanes, MX compounds, haloamides, haloacetonitriles, halopyrroles, nitrosamiones, and aldehydes. The concentration of these DBPs ranges between sub- $\mu\text{g/l}$ and mid- $\mu\text{g/l}$ levels.

Preventing or reducing the formation of threatening DBPs is required. Ozonation is one used method, which offers additional oxidation potential. However, ozone is a very selective oxidant that preferentially reacts with double bounds and activated aromatic systems with hydroxyl or amino groups, whereas highly halogenated compounds, with low electron densities at the carbon centre, are less affected [4]. Additionally, ozonation does not totally mineralize the organic matter and organic acids, aldehydes or carboxyaldehydes are formed [5]. Furthermore, ozone may oxidise bromide ions leading to the formation of bromated THMs and other organic by-products, as well as that ozone can oxidize the disinfectants [5].

Other promising technologies are advanced oxidation processes (AOP). The main reactive species is the OH-radical. OH-radicals are fast oxidants and less selective in comparison to ozone.

Glauner and Frimmel applied ozone-based advanced oxidation processes for the treatment of swimming pool water [6]. They found that peroxone and UV/O₃ were superior to ozonation and that the peroxone

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process (O_3/H_2O_2) is most promising. The application of peroxone process led to a net decrease of DBP formation. However, especially for the UV/ O_3 treatment a slight increase of the trihalomethane formation was observed. Recently, experiments were conducted for improving the quality of drinking water by photocatalysis using UV and artificial sun light, whereas they found that artificial sunlight was not sufficient to decompose humic substances [7].

In the current research, photolytic and photocatalytic swimming pool water treatment was investigated by the irradiation with medium-pressure-mercury lamp, UV light emitting diodes (UV-LEDs), and solar irradiation. The medium-pressure-mercury lamp has the advantage that it emits strongly between 200 and 400 nm. Especially wavelengths between 200 and 300 nm are appropriate for the photolysis of halogenated aliphatic compounds [8]. The photolysis of C-Cl bonds occurs at wavelengths between 210 and 230 nm and of C-Br bands at 250 nm leading to the formation of chloride and bromide ions [8]. Furthermore, it also emits at germicidal wavelength of 254 nm at which DNA strongly absorbs and most germs are killed or rendered inert. The disadvantage of medium-pressure-mercury lamp is that it suffers lumen depreciation and thus it has to be replaced after ~9000 hrs by a new lamp, which is costly. UV-LEDs do not suffer lumen depreciation and have a high luminous efficacy. However, the light intensity of UV-LEDs is very low in comparison to medium-pressure-mercury lamps, thus many UV-LEDs are required for irradiation. UV-LEDs emit light at a certain wavelength which is eligible to excite photocatalysts like TiO_2 . On the other hand side, solar irradiation is a free accessible resource, which consists of up to 5% of UV and it would be ecologically beneficial to utilize sun irradiation for the treatment of water.

2. Experimental Procedure

2.1. Materials and Methods

The samples were received from the swimming pool of the Gdansk University of Technology. Aeroxide TiO_2 -P25 was used as photocatalyst. The concentration of photocatalyst was 0 g/l, 1.5 g/l, and 3.0 g/l for all experiments. Two different reactors were used for the experiments. For the experiments with medium-pressure-mercury lamps and UV-LEDs, the photoreactor was a batch reactor with an immersed quartz tube in the center, which contained the UV irradiation source. The two UV irradiation sources were in detail a 150 W medium-pressure-mercury lamp and twenty 14 mW UV-LEDs ($\lambda=375$ nm). The volume of the reactor was 0.7 l and the solution was continuously stirred. The samples were aerated before the experiments and the temperature was maintained at 20 °C. The UV-flux was measured with a UV-power meter (Hamamatsu Photonics, measuring range 310 nm to 380 nm).

For the experiments with solar irradiation, a special constructed solar photoreactor was used, which consisted of in series connected quartz tubes (i.d. 40 mm) positioned over a parabolic mirror. The volume of the reactor is 4 l and the photocatalyst slurry was pumped with 5.1 l/min in a loop. The suspension was aerated ensuring that enough oxygen was dissolved. The experiment was carried out at ambient temperature. The solar radiation flux density was measured with a pyranometer.

The photocatalytical decomposition of organic matter was analyzed by the liquiTOC from Elementaranalysen GmbH determining the total organic carbon (TOC) concentration. The advantage of total organic carbon determination is that it serves as sum parameter and covers all organic compounds and DBPs in the water.

2.2. Results and Discussion

The average starting TOC concentration for all experiments was determined with 6.33 mg/l with maximum value of 10.44 mg/l and minimum value of 4.7 mg/l.

The UV-flux of the medium-pressure-mercury lamp was determined with 505 W/m^2 and the irradiated area was 131.3 cm^2 . The decrease of the TOC for different photocatalyst concentrations is summarized in Fig. 1. When the swimming pool water was irradiated for 60 min by the medium-pressure-mercury lamp, 46% of the organic carbon was decomposed by photolytic reactions. Photocatalyst addition increased the decomposition ratio to 66% and 68.5% for 1.5 g/l and 3.0 g/l TiO_2 , respectively. Thus, the decomposition rate increased only slightly with increasing photocatalyst concentration. It can be concluded that the decomposition of organic compounds is caused by photolytic and photocatalytic reactions.

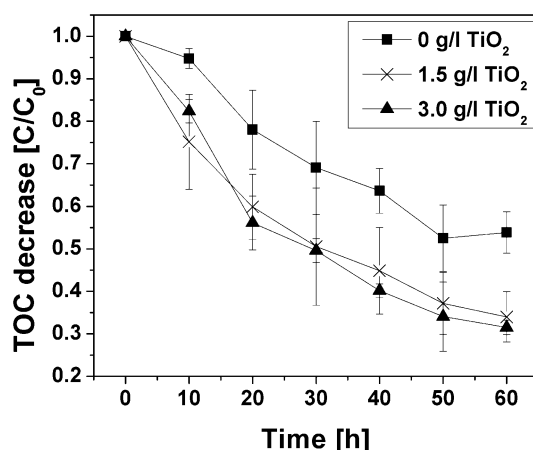


Fig. 1: TOC decrease of swimming pool water irradiated by medium-pressure-mercury lamp in dependence of TiO₂ photocatalyst concentration.

The average UV-flux of the UV-LEDs was determined with 53 W/m² and the irradiated area was 11.5 cm². Thus, the UV-LEDs have an 9.5 lower UV-flux than in comparison to the medium-pressure-mercury lamp. For this reason, the samples were irradiated for 300 min to determine a decrease of the TOC concentration. When no photocatalyst was present, only a slight decrease of TOC was observed, which can be caused by the evaporation of volatile organic compounds. Thus, it can be concluded that no photolytic decomposition took place. This was expected, since the UV-LEDs emit at 375 nm. The addition of 1.5 g/l TiO₂ lead to 17.5% decrease of the TOC and 3.0 g/l of TiO₂ yielded in a similar decrease of the TOC of 17.1% after 300 min irradiation (see Fig. 2).

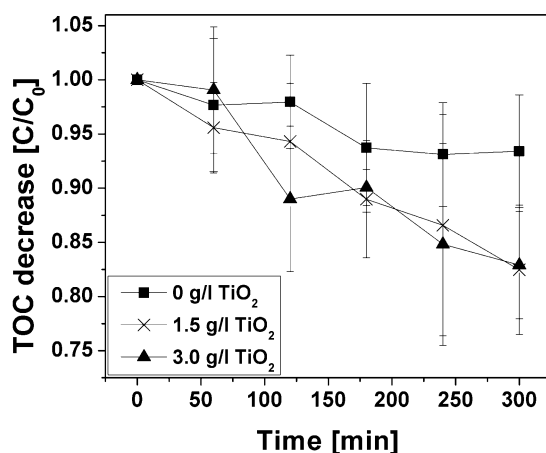


Fig. 2: TOC decrease of swimming pool water irradiated by UV-LEDs in dependence of TiO₂ photocatalyst concentration.

From Fig. 3 it can be seen that the solar irradiation of the swimming pool water for up to 5.5 hrs does not decrease the TOC concentration. The slight change of TOC can be explained by statistical deviations of the measurement. Addition of photocatalyst yields in the decrease of TOC. The initial TOC concentration was 5.4 mg/l and 6.6 mg/l for the 1.5 g/l and 3.0 g/l photocatalyst suspensions, respectively. The solar irradiation changed depending on the cloudiness, which is shown in Fig. 4 and Fig. 5. For both 1.5 g/l and 3.0 g/l photocatalyst suspensions a decrease of the TOC was observed, whereupon it is not possible to draw a final conclusion about the influence of photocatalyst concentration, since the irradiation of the sample varied. For the 3.0 g/l photocatalyst suspension, the decrease of TOC begins with a delay but reaches in half of the time similar TOC decreasing rate as in comparison to the 1.5 g/l photocatalyst suspension. A possible explanation can be the higher TOC value for the 3.0 g/l photocatalyst suspension, which delays the initialization of the

decomposing reactions but also gives a higher decreasing rate, since more organic material can be decomposed. To investigate, if some of the organic compounds adsorb on the TiO_2 surface and influence the TOC measurement, an experiment without irradiation was carried out (Table 1). It can be seen, that no decrease of TOC occurred, which means that the TOC value is not influence by adsorption phenomena.

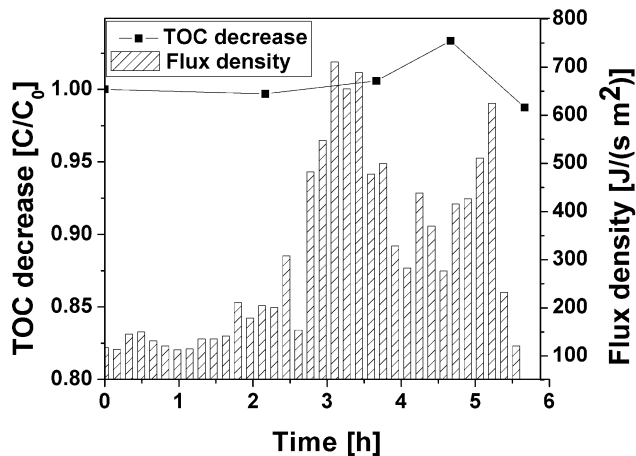


Fig. 3: TOC decrease for solar irradiation of swimming pool water without TiO_2 .

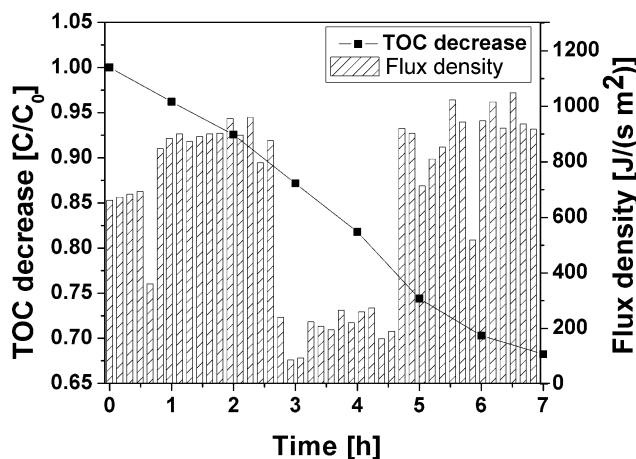


Fig. 4: TOC decrease for solar irradiation of swimming pool water with 1.5 g/l TiO_2 .

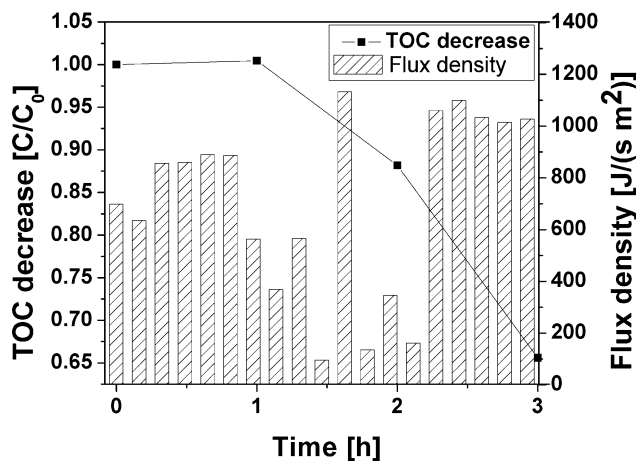


Fig. 5: TOC decrease for solar irradiation of swimming pool water with 3.0 g/l TiO_2 .

Table 1: Change of TOC concentration of 1.5 g/l TiO₂ swimming pool water suspension without irradiation.

Sample	Time	TOC	TOC decrease
[-]	[h]	[mg/l]	[C/C ₀]
1	0	5.21	1.00
2	1	5.24	1.01
3	2	5.49	1.05
4	2.5	5.23	1.00

3. Conclusions

It has been shown that the usage of TiO₂ photocatalyst is applicable for the treatment of swimming pool water. However, the decomposition of organic compounds depends on the applied UV irradiation source. The swimming pool water treatment by the mercury-medium-pressure lamp showed decrease of the TOC also without photocatalyst. Organic compounds are decomposed by photolytic reactions, since the mercury medium pressure lamp emits strongly between 200 and 400 nm. Addition of photocatalyst increased the decrease of TOC by photolytic and photocatalytic reactions. The treatment of swimming pool water by UV LEDs without photocatalyst showed no decrease of the TOC since no photolytic reactions took place. A slight decrease of the TOC can be observed when TiO₂ was added, which means that UV-LEDs are capable to excite the photocatalyst TiO₂. However, the radiant emittance of the UV-LEDs is low in comparison to mercury-medium-pressure lamp and thus only a marginal decrease of TOC over 300 min irradiation time is observed. Solar irradiation was also capable to decompose organic compounds. However, the irregular irradiation of the sample and the low UV fraction of sun light leads to long irradiation times. An effect of increasing the photocatalyst concentration from 1.5 to 3.0 g/l was not observed. For the experiments with the mercury-medium-pressure lamp and the UV-LEDs the decomposition rate was similar for these concentrations. Finally, it can be concluded that the mercury-medium-pressure lamp is still superior in comparison to UV-LEDs and solar irradiation.

4. References

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